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THE EFFECT OF WATER VAPOR ON FLAME VELOCITY IN EQUIVALENT CO-O$_2$ MIXTURES

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SUMMARY

This investigation, carried out at the National Bureau of Standards at the request and with the financial assistance of the National Advisory Committee for Aeronautics is a quantitative study of the effect of water vapor upon the spatial speed of flame in equivalent mixtures of CO and O$_2$ at various total pressures from 100 to 760 mm Hg. These results show that, within this pressure range, an increase in flame speed is produced by increasing the mole fraction of water vapor at least as far as saturation at 25° C., and that the rate of this increase is greater the higher the pressure. It is evident that water vapor plays an important part in the explosive oxidation of CO; the need for further experimental evidence as to the nature of its action is indicated.

INTRODUCTION

The explosive reaction between CO and O$_2$ was the subject of a detailed investigation at the National Bureau of Standards by the late F. W. Stevens. As a result of his earlier work by the Bunsen-Gouy burner method, he pointed out (reference 1) that "with reduction of the partial pressure of water vapor in the explosive mixture, the rate of flame propagation is reduced until a point is reached where the explosive reaction cannot be induced in the gases."

The difficulty of initiating explosive reaction by passing a spark through a dry mixture of CO and O$_2$ has long been known. A comprehensive review of this subject is given by Bone and Townend (reference 2). In the present investigation difficulty was experienced in igniting even imperfectly dried mixtures at low pressures, but primary attention was given to the effect upon the speed of the reaction zone in space of varying the concentration of water vapor in the range where ignition could be readily attained.

Such a quantitative survey is desirable, not only for the information it may yield relative to the mechanism of the reaction, but also to serve as a guide in its further study. These results are essential if the soap-bubble, or constant-pressure method, developed and used by Stevens (reference 3), is to be employed. In this method the presence of water vapor cannot be avoided, and means must therefore be found for controlling its concentration. The results of the present investigation show the extent to which this control of the water-vapor content of an explosive mixture must be governed, in order that a precise value of flame speed may be measured by the bubble method. The goal of these measurements was the quantitative determination of the effect of varying the concentration of water vapor in chemically equivalent mixtures of CO and O$_2$ upon the speed of propagation of flame, in space, in the range of pressures from 100 to 760 mm Hg.

METHOD

The method chosen for the present investigation required photographs of the travel of the reaction zones. For this reason, and to provide for accurate control and variation over wide limits of the quantity of water vapor, these experiments were performed in closed glass vessels (i. e., at constant volume). The first series was carried out in a relatively large (5-liter) spherical glass flask. Throughout this series it was found that the speed of the flame was not appreciably influenced by the rising pressure until approximately four-fifths of the diameter of the flask had been traversed. In other words, under the conditions of this set of experiments, the flame front travels for a considerable distance at a practically constant spatial velocity.

Similar experiments at a dry-gas pressure of 760 mm were performed in a Pyrex glass cylinder 6 inches in diameter and 6 inches tall, with metal disks sealing the ends through rubber gaskets. In this series the effect of increasing pressure became apparent when about one-half the diameter of the cylinder had been traversed. That is, the flame velocity remained practically constant while the flame traveled about 1½ inches from the spark gap. This amount proved adequate for the satisfactory calculation of flame speed from the photographs.

A chemically equivalent mixture of CO and O$_2$, containing a known amount of water vapor, was intro-

duced into the appropriate glass-explosion vessel. A photograph of the travel of the reaction zone across the horizontal mid-section of the explosion vessel was taken on a moving film. Simultaneously time signals were recorded on the film. The speed of the flame front in space can be computed from measurements of the dimensions of such a photographic record when the ratio of the size of the object to the size of the image is known.

A comparable value of the speed of flame in space may also be measured by the soap-bubble method for mixtures high in water content. The agreement of such values obtained by the two methods will be shown in a later report.

PREPARATION AND PURIFICATION OF THE GASES

Carbon monoxide was prepared in a glass system according to the general method outlined by Thompson (reference 4). Formic acid was slowly dropped into concentrated phosphoric acid at a temperature between 160° and 170° C. The gas liberated was led through a water-cooled condenser, the inner tube of which was bathed with a thin stream of concentrated KOH solution to remove CO_2. The wet CO then passed to a liquid air trap where water and residual CO_2 were removed. Glass wool in this trap prevented the entrainment of ice particles in the gas stream. Thence the CO was led through a drying tube filled with glass wool and P_2O_5. The dry gas was collected in glass flasks that had been previously evacuated.

The oxygen used in the experiments at pressures below atmospheric was obtained from a commercial high-pressure cylinder and was passed at reduced pressure through a liquid air trap and P_2O_5 tube similar to those used for the CO. Electrolytic O_2 from which the H_2 was removed by passage over hot copper oxide, was used in the experiments at one atmosphere. Drying was accomplished as in the other cases, with liquid air and P_2O_5.

APPARATUS

The 5-liter explosion vessel was made from a spherical flask of Pyrex glass that had been carefully annealed. The spark gap at its center consisted of two tungsten wires, insulated from each other and from the explosive mixture by capillary tubes which were sealed to the tungsten about 5 mm from the gap. The gap itself was about 2 mm wide. The electrode assembly was sealed through an appropriate neck in the flask by a beeswax-rosin cement.

The explosion vessel capable of withstanding the maximum pressures developed when the initial pressure of the mixture of CO and O_2 was 760 mm, consisted of a heavy-walled Pyrex cylinder, 6 inches in diameter and 6 inches tall. The ends were closed with metal plates and sealed with rubber gaskets. The 0.5 mm spark gap, formed by two small nickel spheres sup-

ported by nickel wires, was located at the center of the glass cylinder. The bottom metal plate supported the spark gap and a small needle valve through which the gases were transferred.

From each of the explosion vessels a tube led to a manifold through which connections could be made to any of the following: (1) a high-speed mercury vapor pump; (2) a small vessel containing distilled water at a controlled temperature; (3) the storage flasks containing dry CO and O_2; and (4) a mercury manometer.

For protection in case of accidental disruption of the glass, the 5-liter explosion vessel was placed within a heavy cast-iron sphere and the cylindrical vessel within a section of 8-inch iron pipe. An opening was provided in each at the level of the spark gap. Neither of the glass vessels failed in service.

Mercury-in-glass "calorimetric standard" thermometers were used for measuring temperatures and a closed-end mercury manometer for observing pressures. The capillarity and scale displacement correction for the manometer was measured by direct comparison with a barometer and all manometric observations were corrected to mercury at 0° C. and standard gravity. It is believed that the observed values of temperature and pressure, which were used primarily in calculating the composition of the mixtures, are in error by less than 0.3° C. and 0.5 mm of mercury, respectively.

The photographic recording equipment, which is mounted as a unit on a portable table, consists of a camera, a spark-timing device, a firing mechanism, and apparatus for recording time signals on the moving films. The camera lens (Zeiss Tessar f 1:4.5) has a focal length of 18 cm and, during these experiments, was at a distance of 100 cm from the spark gap. The film is carried on a cylindrical drum of 10 cm diameter, which can be rotated at the desired constant speed. A slit about 1 mm wide, extending across the entire drum, is located just in front of the film. A shutter, operated by a relay, permits or prevents passage of light through the slit. The shaft bearing the drum also operates a mechanical device by means of which an electric contact can be made for a chosen fraction of a revolution of the drum. This contact controls the operation of the relay which opens and closes the shutter and which also permits the firing spark to jump at the instant the shutter is fully open.

The firing mechanism consists of a bank of telephone condensers (about 18 microfarads capacity) which are charged to 220 volts through the building supply mains and which, upon action of the relay, discharge through the primary of an induction coil. The current induced in the secondary then passes across the spark gap.

The time signals are recorded as short dashes on the film, by means of a shutter operated by a tuning fork having a frequency of approximately 250 cycles per

second. Vibration of the fork is induced and maintained by an appropriate vacuum-tube installation. The shutter operated by the fork is illuminated by a carbon arc.

Previous to making each series of observations, a scale set at the position later to be occupied by the spark gap was photographed with the drum of the camera stationary. From such photographs the ratio of the size of the object to the size of the image was determined.

PROCEDURE

The usual procedure in filling an explosion vessel was as follows. It was first evacuated to a residual pressure of 0.001 mm or less. Connection was then made to the water reservoir, the temperature of which was maintained at a previously chosen value within a vacuum vessel. Fifteen minutes were usually allowed for filling the explosion vessel with water vapor at a pressure determined by the temperature of the reservoir, though test experiments indicated that equilibrium was established in about 2 minutes. The temperatures of the reservoir and explosion vessel were recorded, the latter was closed off, the line was evacuated, and the dry CO admitted to a previously chosen pressure as indicated by the manometer.

When the temperature of the water reservoir, and hence also the pressure of the water vapor in the explosion vessel, were known, a simple calculation was made to find the values of pressure of H_2O+CO and $H_2O+CO+O_2$ that were required if the final mixture was to contain CO and O_2 in equivalent proportions at a chosen total pressure. Practically, small variations from equivalence are of no importance because the rate of change of flame speed with composition is very small in this region.

After a steady state was reached by the mixture of H_2O and CO, its temperature and pressure were recorded, and dry O_2 was admitted to the previously calculated pressure. At least 1 hour was then allowed for complete mixing before the temperature and pressure were observed and the mixture fired.

The sequence of events observed in taking a record of an explosion will now be recounted. The explosion vessel was charged as described with a mixture of CO, O_2, and H_2O vapor of known proportions and total pressure. The room was darkened and the film attached to the camera drum, which was then rotated at a chosen constant speed. The tuning fork was set into vibration and the arc light turned on. An auxiliary switch was closed manually to complete the circuit to the gap except for the contact operated by the drum through the relay. Since this latter contact is made only once in 96 revolutions of the drum, ample time was afforded to close and reopen the manual switch in such a way that the camera shutter was operated but a single time. When contact was made by the rotating mechanism, the relay opened the

shutter and fired the charge. When contact was broken by further revolution of the shaft, the shutter was closed again. While the film was being developed and fixed the explosion vessel was evacuated, preparatory to recharging.

RANGE OF THE MEASUREMENTS

Previous experience indicated that the active gases in equivalent proportions at initial pressures up to 300 mm could be exploded in the 5-liter glass vessel without disrupting it. This supposition proved correct, but this vessel was not subjected to higher pressures because of the hazard incident to disruption. At pressures lower than 100 mm the actinic light from the explosions was not sufficiently intense to give satisfactory photographs. Measurements in the 5-liter vessel were therefore confined to the range 100 to 300 mm of mercury. The series made in the cylindrical vessel was carried out at an initial dry-gas pressure of 760 mm.

The water-vapor content in each case was varied over the range which was practical for work at atmospheric temperature. Table I shows the limits for these ranges of water-vapor concentration.

TABLE I.—RANGES OF WATER-VAPOR CONCENTRATION

Initial dry-gas pressure	Mole fraction of water vapor	
mm Hg	Minimum	Maximum
100	0.028	0.182
150	.006	.130
200	.004	.102
300	.002	.071
760	.0014	.030

The upper limit was in each case determined by the saturation pressure of water vapor at the temperature of the explosion vessel (i. e., room temperature). The lower limit was determined by the ignitibility of the mixtures and by the amount of actinic light emitted.
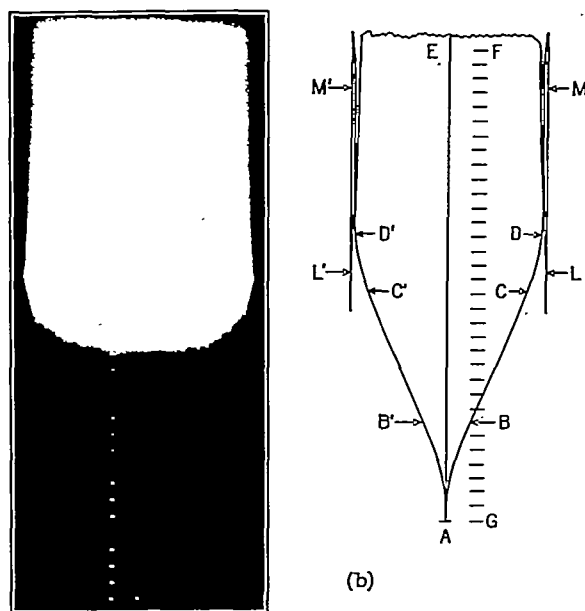
RESULTS OF THE MEASUREMENTS

Figure 1 (a) is a reproduction of a typical record obtained from an explosion in the 5-liter flask by the method which has been described. Figure 1 (b) is a diagrammatic representation of this same record illustrating the details of the interpretation that was applied to all the records.

The image of the igniting spark is shown at A. After ignition the records at pressures below one atmosphere show, without exception, that the flame front moves for a time with a positive acceleration, as indicated by the curved traces AB and AB'. At B and B' its speed has reached a value that remains practically constant until the points C and C' near the walls of the vessel are reached. This constancy is apparent from the fact that the traces BC and B'C'

are straight lines on a film that traveled at constant speed. The actual value of this constant speed can be calculated from the angle between the traces BC and B'C', the speed of the film, and the magnification factor of the camera. The row of dashes FG represents the time record and gives directly the speed of the film, since, from the calibration of the tuning fork, the distance between successive dashes is known to represent the travel in $\frac{1}{495}$ second.

At C and C' the acceleration of the flame front changes from zero to a negative value as the walls of the vessel (LM and L'M') are approached. At D and D' the flame reaches the walls of the vessel, and the tangent of the angle of approach should be a measure of the speed of the flame front relative to the active gases at the maximum pressure. Attempts to

(a) Typical record of the explosion.   (b) Diagrammatic representation of record shown in (a).

FIGURE 1.—An explosion of a mixture of CO, O₂, and water vapor at constant volume.

measure this angle have not yielded results of sufficient precision to be worthy of record.

After the flame reaches the walls of the vessel there is still sufficient actinic light being emitted by the hot gases to form a comparatively long trace on the film. This trace, which is not completely shown in the figure, gradually decreases in intensity as the gases lose heat to the walls.

The line AE is the image left on the film by the sparking device.

The records taken of explosions in the cylindrical vessel are similar to that shown in figure 1, except that the traces left by the flame front are straight from the spark until the effect of pressure begins to show at about one half the total travel.

Figure 2 shows graphically the effect of water vapor on the speed of flame in space during that interval in which it is constant for any given mixture (i. e., the

values, obtained from the traces BC and B'C', fig. 1). It is evident that the speed of flame is greatly influenced by the amount of water vapor present at each of the dry-gas pressures studied. It is also apparent that the effect of changing the amount of water vapor from any one mole fraction to another is greater the higher the dry-gas pressure, since the curves become increasingly steep with increasing pressure. It is clearly demonstrated, therefore, that at atmospheric pressure the water-vapor content must be very carefully controlled and specified if determinations of flame speed in mixtures of CO and O₂ are to be significant.

In figure 2 it is also noteworthy that, with the possible exception of the 100 mm pressure curve which was actually followed to higher water concentrations than shown, the water vapor always exerted some influence that produced higher flame speeds with increasing water concentration. There is undoubtedly some concentration of water at every dry-gas pressure for which the speed will reach a maximum and beyond
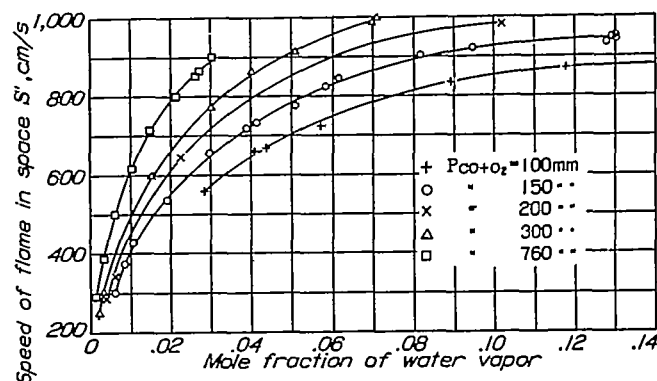

FIGURE 2.—The effect of water vapor on the speed of flame in space in equivalent mixtures of CO and O₂.

which it will begin to decrease, i. e., beyond which at least a part of the water will behave as a diluent. Though the concentration of the water could not be increased to this maximum value for pressures above 100 mm, it was probably reached and perhaps slightly surpassed at this pressure. Extrapolation of the data embodied in figure 2 indicates that, if explosions at 50 mm pressure could have been satisfactorily recorded, this maximum would have appeared when the mole fraction of water reached about 0.14, and that the speed beyond this point would have decreased with further addition of water vapor. If it had been practicable in the present apparatus to maintain the explosion vessel at elevated temperatures, it is believed that this maximum might have been observed at each of the dry-gas pressures studied.

Examination of the photographic records yields several points of interest with regard to the time required for the attainment of constant speed after ignition (i. e., the period of acceleration). It is possible to get an approximate value of the duration of the period of acceleration from each of the records. The

following conclusions have been drawn from an assembly of such data: (1) If the mole fraction of water vapor is kept constant and the dry-gas pressure is varied, the acceleration period decreases with increasing pressure in a practically linear fashion. Extrapolation indicates that at pressures above 450 mm, the acceleration period would become vanishingly small. Actually none has been observed when an equivalent mixture of the gases is fired at atmospheric pressure. (2) If the dry-gas pressure is kept constant and the concentration of water vapor is varied, the acceleration period decreases with increasing water content, within the range of these experiments. The rate of decrease is much more rapid in the range of low-water concentration.

In general, for the range covered by these experiments, ignition could be accomplished more easily the higher the water content of the mixtures and the higher the total pressure. It seems also to be generally true that, for a given dry-gas pressure, darker negatives (more actinic light) were obtained when the water content was high. The negatives were not always developed under identical conditions, but an effort was made to carry the development of each as far as possible without fogging.

All efforts to ignite the dry gases, prepared in the manner already described, by passage of sparks from the induction coil have been unsuccessful. In the early stages of the project, a spark gap consisting of two 1 mm balls of Pt suspended by 0.1 mm Pt wires was used. With this gap also, the induction-coil discharge failed to ignite the dry charge. A single explosion was produced in a dry mixture at 250 mm pressure after passage of a large number of sparks, produced with a high-tension magneto. An attempt was made to repeat this experiment at 75 mm pressure. Under the repeated sparking the Pt electrodes were heated to the melting point. One of the small spheres dropped off, but the other remained intact when the magneto was stopped. Instead of cooling down at once, it remained at a visible red heat. Its temperature decreased slowly during an interval of about 1 hour, at the end of which time it was still readily visible in the dark room. Then it suddenly ceased to glow, and the pressure in the explosion vessel became constant at 56 mm. The slow oxidation, catalyzed by the hot Pt, liberated sufficient energy to keep the Pt in the active state until the oxidation of the CO was approximately 80 percent complete.

The observed values of the speed of flame in space, as well as of the speed of flame relative to the active gases and of expansion ratio, which will be described in a later paper, are believed to be characteristic of the particular mixtures for which they were measured. Any interpretation involving these observed quantities must, however, take cognizance of the fact that the loss of energy by radiation may be one of the several factors that together determine the speed with which reaction can progress. For example, if it should be subsequently demonstrated that, at constant dry-gas pressure, the total energy lost by radiation varied considerably with the concentration of water vapor, a more precise interpretation of the curves given in figure 2 would be possible. At present, however, there are no data available by means of which the effects of water vapor and radiant-heat loss can be separated. It is not anticipated that the actual value of the energy lost by radiation will prove to be a large fraction of the total chemical energy involved, nor that large variations in radiant-heat loss with composition will be found. For the present it therefore seems expedient in all the computations of this report to neglect the heat lost by radiation, with the idea that appropriate corrections can be applied when the need for and magnitude of such corrections has been found.

CONCLUSIONS

1. Throughout the entire range of these measurements an increase in the mole fraction of water vapor is accompanied by an increase in the linear rate of propagation of flame in space for equivalent mixtures of CO and O₂ at constant initial pressure.

2. This rate of increase of speed with the mole fraction of H₂O becomes greater as the pressure of the reactants is raised.

3. Despite some experimental evidence to indicate that the presence of water vapor is not essential for the production of CO₂ by the reaction of CO and O₂, there can be little doubt that the water is an essential factor in the attainment of complete equilibrium during their explosive combination.

4. The effect of water vapor is of sufficient magnitude to make essential the accurate control and specification of water-vapor content in any study involving the measurement of flame speed in the explosive oxidation of CO.

5. Experiments by the soap-bubble method cannot be expected to yield precise results unless the concentration of water vapor is very carefully controlled.

6. The results of the present series have aided materially in planning the future course of the study of gaseous explosive reactions. They have been of especial value in the development of the refinements that seem essential to the successful determination of flame speed by the soap-bubble method.

NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C., *January 10, 1935.*

REFERENCES

1. Stevens, F. W.: The Rate of Flame Propagation in Gaseous Explosive Reactions. Amer. Chem. Soc. Jour., vol. 48, no. 7, 1926.
2. Bone, William A., and Townend, Donald T. A.: Flame and Combustion in Gases. Longmans, Green & Co., Ltd., (London), 1927, chs. XXIV and XXVII.
3. Stevens, F. W.: A Constant Pressure Bomb. T. R. No. 176, N. A. C. A., 1923.
   Stevens, F. W.: The Gaseous Explosive Reaction—The Effect of Inert Gases. T. R. No. 280, N. A. C. A., 1927.
   Stevens, F. W.: The Gaseous Explosive Reaction—A Study of the Kinetics of Composite Fuels. T. R. No. 305, N. A. C. A., 1929.
   Stevens, F. W.: The Gaseous Explosive Reaction at Constant Pressure—The Reaction Order and Reaction Rate. T. R. No. 337, N. A. C. A., 1929.
   Stevens, F. W.: The Gaseous Explosive Reaction—The Effect of Pressure on the Rate of Propagation of the Reaction Zone and upon the Rate of Molecular Transformation. T. R. No. 372, N. A. C. A., 1930.
4. Thompson, J. G.: Pure Carbon Monoxide for Experimental Purposes. Indus. and Engr. Chem., vol. 21, no. 4, 1929.